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(54) Copolyester, polyester composition containing the copolyester, and polyester laminated structure having layer composed of the copolyester or the polyester composition.

(57) A copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units; a gas barrier imparting agent composed of the copolyester; a polyester composition composed of (A) a polyethylene terephthlate and (B) the copolyester; and a film, a preform and a container composed of the polyester composition. Also provided are a polyester laminated structure, a stretched laminated structure, a preform and a laminated blow-molded article each composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer composed of the copolyester or the polyester composition.

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formed from it.

Japanese Laid-Open Patent Publication No. 64658/1984 proposes a method of blending polyethylene isophthalate and polyethylene terephthalate.

However, the polyethylene isophthalates described in the above-cited patent documents contains high-melting oligomers, and these oligomers adversely affect the physical properties of the resulting molded articles.

To improve the gas-barrier property of PET, a copolyester was proposed which is prepared by copolymerizing isophthalic acid as a dicarboxylic acid component and ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene as a dihydroxy compound component (see Japanese Laid-Open Patent Publication No. 167617/1983).

If an article such as a container is molded from a polyester resin containing moisture, hydrolysis takes place and the mechanical properties of the molded article are degraded. It is necessary therefore to dry the polyester resin before molding. However, since an isophthalate-type copolyester containing a large amount of isophthalic acid as the dicarboxylic acid component has a lower crystallinity and glass transition temperature (Tg) than a terephthalate-type copolyester, it can be dried only at low temperatures. Accordingly, to obtain an isophthalate-type polyester having a low water content, long periods of time are required for its drying. If the isophthalate copolyester is dried at temperatures higher than the glass transition temperature, the copolyester will melt-adhere to itself.

Usually, polyethylene terephthalate is dried at a temperature of 110 to 160 °C. If the polyethylene terephthalate dried at the above temperatures and the isophthalate-type copolyester dried at lower temperatures are dry-blended immediately after drying, the isophthalate-type copolyester will be heated to a temperature higher than the glass transition temperature by the polyethylene terephthalate which is still at a considerably high resin temperature. Consequently, the pelletized isophthalate-type copolyester will get out of shape or the copolyester pellets melt-adhere to one another. Consequently, it is difficult to mix them uniformly.

For this reason, it has been desired to develop an isophthalate-type copolyester having a high glass transition temperature (Tg) and excellent thermal resistance.

An isophthalate-type copolyester having copolymerized therein bis(4-beta-hydroxyethoxyphenyl)sulfone was proposed as a copolyester having a high glass transition temperature (Tg) (see Japanese Laid-Open Patent Publication No. 167617/1983).

The use of bis(4-beta-hydroxyethoxyphenyl)sulfone makes the isophthalate-type copolyester slightly higher in glass transition temperature (Tg), but its Tg elevating effect is not sufficient. In addition, if its gas-barrier property is degraded, or the copolyester is colored or the monomeric components bleed out, the polyester is undesirable in view of food sanitation.

SUMMARY OF THE INVENTION

It is an object of this invention to solve the above problems in the prior art, and to provide an isophthalate-type copolyester being free from high-melting oligomers and having a high glass transition temperature and excellent gas-barrier property and surface properties.

Another object of this invention is to provide a gas-barrier property imparting agent comprising the above isophthalate-type copolyester. Another object of this invention is to solve the problems associated with the prior art discussed above, and to provide a polyester composition which does not contain high-melting oligomers, can be dried at a high speed and has excellent thermal resistance, impact strength, surface properties, transparency and gas-barrier properties.

Another object of this invention is to provide a film, a preform and a container composed of the above polyester composition.

Another object of this invention is to solve the problems associated with the prior art discussed above, and to provide a polyester laminated structure which is free from high-melting oligomers, and has excellent moldability, stretchability, gas-barrier property, especially with respect to oxygen and carbon dioxide gas, thermal resistance, impact strength, surface properties, transparency, electrical properties and chemical resistance.

Another object of this invention is to provide a stretched laminated structure, a preform for blow molding and a laminated blow-molded article each composed of the above polyester laminated structure and having excellent gas-barrier property, especially with respect to oxygen and carbon dioxide gas, thermal resistance, impact strength, surface properties, transparency, electrical properties and chemical resistance.

The above objects are achieved in accordance with this invention by a copolyester having an intrinsic

dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The copolyester of this invention is characterized in that the dicarboxylic acid units (recurring units derived from a dicarboxylic acid) consist of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and the dihydroxy compound units (recurring units derived from a dihydroxy compound) consist of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, and that it has an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g.

Since the copolyester of the invention uses isophthalic acid units and 2,6-naphthalenedicarboxylic acid units as the dicarboxylic acid units and ethylene glycol units and 1,3-bis(2-hydroxyethoxy)benzene units as the dihydroxy compound units, it does not contain high-melting oligomers and has excellent gas-barrier property and surface properties and a high glass transition temperature.

The copolyester of this invention will be described below specifically.

The copolyester of the invention can be obtained by co-condensation reaction of the following dicarboxylic acids and dihydroxy compounds.

The dicarboxylic acids used in this invention are 95 to 60 mole %, preferably 90 to 70 mole %, of isophthalic acid, and 5 to 40 mole %, preferably 10 to 30 mole %, of 2,6-naphthalenedicarboxylic acid.

If the isophthalic acid is used in an amount of more than 95 mole %, the resulting copolyester does not have so high a glass transition temperature. If it is used in an amount of less than 60 mole %, the glass transition temperature of the resulting copolyester has too high a glass transition temperature, and a blend of the resulting copolyester and polyethylene terephthalate, or a multilayer laminate of the copolyester cannot be sufficiently stretched.

In the present invention, another dicarboxylic acid may be used in addition to the isophthalic acid and 2,6-naphthalenedicarboxylic acid in an amount which does not impair the properties of the resulting copolyester. Examples of the other dicarboxylic acid are terephthalic acid, phthalic acid, and 2-methylterephthalic acid. As the dihydroxy compounds, ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene are used in the invention. These dihydroxy compounds are used in such amounts that the hydroxy compound component consists of 95 to 70 mole %, preferably 90 to 80 mole %, of ethylene glycol, and 5 to 30 mole %, preferably 10 to 20 mole %, of 1,3-bis(2-hydroxyethoxy)benzene. By using ethylene glycol and 1,3-bis-(2-hydroxyethoxy)benzene in the above amounts as the dihydroxy compounds, a copolyester being free from high-melting oligomers and having excellent surface properties and a high glass transition temperature can be obtained.

In addition to ethylene glycol and 1,3-bis(2-hydroxyethoxy)benzene, another dihydroxy compounds may be used in an amount which does not impair the properties of the resulting copolyester. Examples of the other dihydroxy compound include dihydroxy compounds having 3 to 15 carbon atoms such as 1,3-propanediol, 1,4-butanediol, neopentyl glycol, cyclohexanediol, cyclohexanedimethanol, 1,4-bis(2-hydroxyethoxy)benzene, 2,2-bis(4-beta-hydroxyethoxyphenyl)propane and bis(4-beta-hydroxyethoxyphenyl)sulfone.

The copolyester of the invention may be composed only of the above dicarboxylic acid units and the above dihydroxy compound units, or of the dicarboxylic acid units, the hydroxy compound units and a small amount of trifunctional or higher polycarboxylic acid units or polyhydroxy compound units. Polycarboxylic acids having 4 to 15 carbon atoms may be used as the trifunctional or higher polycarboxylic acid. Specific examples may be trimellitic acid, trimesic acid and hemimellitic acid. The trifunctional or higher polyhydroxy compounds may be, for example, polyhydric alcohols having 3 to 15 carbon atoms. Typical examples include 1,1,1-trihydroxymethylpropane, glycerol, 1,2,3-butanetriol, 1,2,3-pentanetriol, and pentaerythritol. Polyesters obtained by co-condensing the trifunctional or higher polycarboxylic acid or polyhydroxy compound with the above dicarboxylic acid and dihydroxy compound are preferred because they have improved uniform stretchability in blow molding.

The proportion of the trifunctional or higher polycarboxylic acid units in the copolyester is 0.01 to 2 moles, preferably 0.005 to 1 mole, per 100 moles of the dicarboxylic acid units, and the proportion of the trifunctional or higher polyhydroxy compound units is 0.01 to 2 moles, preferably 0.05 to 1 mole, per 100 moles of the drihydroxy compound units.

The resulting copolyester of the invention has an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g, preferably 0.6 to 1.0 dl/g. If the intrinsic viscosity is less than 0.3 dl/g, the mechanical

container. Where the copolyester is monoaxially stretched, the stretch ratio is usually from 1.1 to 10, preferably from 1.2 to 8, especially preferably from 1.5 to 7. Where the copolyester is stretched biaxially, the stretch ratio is usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the longitudinal direction, and usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the transverse direction. The stretched product may be heat-set according to the purpose for which it is to be used.

As required, the stretched product of the copolyester of the invention may contain suitable amounts of various additives incorporated in conventional polyesters, for example, nucleating agents, inorganic fillers, lubricants, slip agents, antiblocking agents, stabilizers, antistatic agents, antihaze agents, and pigments. The stretched product of the copolyester of the invention may be produced by any of known methods. Generally, a starting molded article such as a film-like material, a sheet-like material or a parison molded from the copolyester or its composition containing the above additives as required is subjected to a stretching treatment, either directly or after it is cooled to a temperature below its glass transition temperature and solidified and then re-heated, at a temperature ranging from its glass transition temperature to its melting point, preferably, from its glass transition temperature to a point 80 °C higher than it. The heat-setting of the stretched product is carried out for a short time at the above stretching temperature or a higher temperature.

If the starting molded article is a film-like article or a sheet-like article, it may be stretched, for example, by a monoaxial stretching method by which it is stretched in one direction, a biaxial stretching method in which it is stretched in the longitudinal direction and then in the transverse direction, a simultaneous biaxial stretching method in which it is stretched in the longitudinal and transverse directions simultaneously, a method by which it is biaxially stretched and then repeatedly stretched in either one direction, a method by which it is biaxially stretched and further in both directions, or a vaccum forming method by which a space between the film- or sheet-like article and the mold is maintained in vacuum to thereby stretch it.

The stretched product of the copolyester may also be produced in the form of a laminate with another resin such as polyethylene terephthalate. Such a laminate may be produced, for example, by a method in which one or more layers of the starting molded article such as a film- or sheet-like article of the copolyester are laminated to one or more layers of a starting molded article such as a film- or sheet-like article of another resin such as polyethylene terephthalate, and the laminate is then stretched, or a method in which a film-or sheet-like article of the other resin is bonded to the stretched product of the copolyester of the invention.

If the starting molded article is a parison, a stretch blow-molded container may be produced from it by stretching the parison at the above temperature in the longitudinal direction, and then blow-molded to stretch it further in the transverse direction (biaxial stretch blow molding). Furthermore, if a parison prepared from one or more layers of the copolyester and one or more layers of the other resin is subjected to the above stretch blow molding, laminated blow-molded article composed of the copolyester and the other resin (e.g., polyethylene terephthalate) can be produced.

Since the stretched product of the copolyester of the invention has excellent gas-barrier property, it can be used in various applications. In particular, biaxially stretched blow-molded containers of the copolyester, because of their excellent gas-barrier property, are useful for holding various articles, for example seasonings, oils, beer, wines and liquors, soft or carbonated drinks such as cola, cider and juices, cosmetics and detergent. Particularly, for holding beer or carbonated drinks, the thickness of the containers can be decreased, and the taste of these goods can be preserved for an extended period of time.

The stretched film of the copolyester of the invention may be used for example, as electrically insulating film, magnetic tapes, photographic films, and metal-vapor deposited films.

The polyester composition of this invention comprises (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester.

The polyester film, polyester preform and polyester container in accordance with this invention are composed of the above polyester composition.

The polyester composition of this invention consists essentially of the polyethylene terephthalate (A) and the copolyester (B). The dicarboxylic acid units of the copolyester (B) are composed of isophthalic acid units and 2,6-naphthalenedicarboxylic acid units and the dihydroxy compound units are composed of ethylene glycol units and 1,3-bis(2-hydroxyethoxy)benzene units. Accordingly, the composition can be dried at a high speed, and had excellent thermal resistance, impact strength, transparency and gas-barrier property. Furthermore, since it does not contain high-melting oligomers, it has excellent surface properties.

Now, the polyester composition, the polyester film, the polyester preform and the polyester container in accordance with this invention will be described in detail.

The polyethylene terephthalate (A) used in the polyester composition of the invention is a crystalline

200 to 600 micrometers.

The stretched film may be a monoaxially or biaxially stretched film. The stretch ratio of the monoaxially stretched film is desirably from 1.1 to 10, preferably from 1.2 to 8, especially preferably from 1.5 to 7. In the biaxially stretched film, the stretch ratio is usually from 1.1 to 8, preferably from 1.2 to 7, especially from 1.5 to 7.

In the biaxially stretched film, the stretch ratio is desirably from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the longitudinal direction, and from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the transverse direction.

The polyester film of this invention can be produced by any known method. Generally, a film-like material molded from the above polyester composition optionally containing the additives, as such or after it is cooled and solidified at a temperature below the glass transition temperature, is re-heated, and this starting molded product is subjected to a stretching treatment at a temperature ranging from the glass transition temperature to its melting point, preferably from the glass transition temperature to a point about 80 °C higher than the glass transition temperature. Heat-setting of the stretched film may be carried out at a temperature higher than the above stretching temperature for a short period.

In the production of the stretched polyester film of this invention, the starting film-like product in the unstretched state may be stretched monoaxially (monoaxial stretching method); stretched in the longitudinal direction and then in the transverse direction (biaxial stretching method); stretched simultaneously in the longitudinal and the transverse directions (simultaneous biaxial stretching method); stretched biaxially and then repeatedly stretching in either direction; stretched biaxially and further in both directions; or may be processed by a so-called vacuum forming method in which a space between the film-like product and a mold is reduced in pressure, thereby to stretch-molding the film-like product.

The polyester composition of this invention may be processed into a sheet-like article substantially in accordance with the methods of producing the polyester film described above.

The polyester preform of this invention may be produced by using the polyester composition.

For example, it may be prepared by injection-molding the polyester composition.

The polyester container in accordance with this invention may be produced by press-forming a sheet of the polyester composition, or stretch blow-molding the polyester preform mentioned above.

Stretch blow-molding may be carried out, for example, by stretching the preform in the longitudinal direction at the stretching temperature for the polyester composition, and then blow-molding it to stretch it also in the transverse direction (biaxial stretch blow molding method).

To produce the polyester container from the biaxial stretch blow molding method, a bottomed preform molded by an ordinary injection-molding machine or a parison obtained by bottoming one end of a parison molded by an extrusion-molding machine is stretched to 1.5 to 3.5 times, preferably 2 to 3 times in the logitudinal direction, and 2 to 5 times, preferably 3 to 4.5 times, in the transverse direction at a stretching temperature of 80 to 120 °C, preferably 90 to 110 °C by a rod moving longitudinally within a blow molding mold and the blowing of a pressurized gas. Molding by an injection molding machine may be carried out by a two-stage method using a cold parison or a one-stage method using a hot parison.

To improve the rigidity of the polyester con tainer, a layer of polyethylene terephthalate may be laminated to the inside and outside layers of the polyester composition.

The polyester container of this invention may be used in various applications because of its excellent transparency and gas-barrier property. In particular, biaxial stretch blow-molded containers have excellent gas-barrier property and transparency and can be used not only for holding seasonings, oils, wines and liquors, cosmetics and detergents, but also holding sparkling drinks such as cola, cider and beer. The polyester containers of the invention permit prolongation of the period within which goods held therein can be taken with their original tastes and flavors without increasing the thickness of the container wall as in conventional containers.

The polyester laminated structure of this invention is composed of (C) a polyalkylene terephthalate layer and (B) a copolyester layer. The copolyester layer (D) is a layer of the copolyester of the invention described hereinabove, or the above polyester composition of the invention comprising the copolyester and polyethylene terephthalate, in which the layers (C) and (D) are stretched.

The preform for the polyester laminated blow-molded product of this invention is composed of (C) a polyalkylene terephthalate and (D) a copolyester layer which is a layer of the copolyester of the invention described hereinabove, or the above polyester composition of the invention comprising the copolyester and polyethylene terephthalate.

The polyester laminated blowmolded product of this invention is composed of (A) a polyalkylene terephthalate and (D) a copolyester layer. The copolyester layer is a layer of the copolyester of the invention described above and the polyester composition of the invention comprising the copolyester and

each of the outside polyalkylene terephthalate layer (C) is usually 50 to 500 micrometers, preferably 50 to 300 micrometers. If the laminated structure is the latter-mentioned three-layer structure, the thickness of the polyalkylene terephthalate interlayer is usually 50 to 500 micrometers, preferably 50 to 300 micrometers, and the thickness of copolyester outside layers (C) is usually 50 to 500 micrometers, preferably 50 to 200 micrometers. When the laminated structure is a multilayer structure, the thicknesses of the intermediate layer and both outside layers of the copolyester (D) and the thicknesses of the intermediate layer and outermost layers composed of the polyalkylene terephthalate layer (C) may be prescribed in the same way as above.

The laminated structure of the invention has excellent stretchability, electrical properties, particularly electrical insulation, mechanical strength, transparency and gas-barrier property.

The polyester stretched laminated structure of the invention may be produced by any known methods. Generally, a starting molded article such as a film or sheet obtained by laminating the polyalkylene terephthalate layer (C) and the copolyester layer (D), either as such or after cooling and solidifying it to a temperature below the glass transition temperature of the polyalkylene terephthalate and the copolyester, is stretched at a temperature above the glass transition temperature of both, preferably 70 to 100 °C.

The polyester stretched laminated molded structure of the invention can be produced by, for example, stretching an unstretched film or sheet (when the starting molded article is film or sheet) is stretched monoaxially (monoaxial stretching method); stretched in the longitudinal direction and then in the transverse direction (biaxial stretching method); stretched biaxially and then repeatedly stretched in either direction; or biaxially stretched and then further stretched in both directions. When the starting structure is to be monoaxially, the stretch ratio is usually from 1.1 to 10, preferably from 1.2 to 8, especially preferably from 1.5 to 7. In the production of the starting molded structure by biaxial stretching, the stretch ratio is usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the longitudinal direction, and usually from 1.1 to 8, preferably from 1.2 to 7, especially preferably from 1.5 to 6, in the transverse direction. The resulting stretched laminated molded structure may be heat-set.

The polyester stretched laminated structure of the invention has excellent mechanical strength, transparency, electrical properties and gas-barrier property. In particular, by using this molded structure for forming electrical and electronic component parts and metallic parts, it is effective for protecting electrical and electronic circuits and preventing corrosion of metals. The polyester stretched laminated structure in the form of a film can also be effectively used for capacitors, motors, transformers and wire and cable coatings by utilizing its electrical properties. Furthermore, by utilizing its excellent gas-barrier property, it may be used as a film for food packaging.

The preform for the polyester laminated blow-molded article of the invention may be produced by using the polyester laminated structure of the invention.

For example, by molding and processing the polyester laminated structure in tubular form, the preform of the invention can be obtained.

The polyester laminated blow-molded article of this invention is a stretch blow-molded article formed from the above polyester laminated structure. The stretched blow-molded article may be produced by stretch blow-molding the above preform.

The polyester laminated blow-molded article may be monoaxially or biaxially stretched. The biaxially stretched polyester laminated blow-molded article has outstanding mechanical strength and gas-barrier property.

The stretch ratios used in the production of the polyester laminated blow-molded article in this invention may be the same as those described above with regard to the stretched polyester laminated structures.

The polyester laminated blow-molded article may be produced by stretching and blow-molding the preform described above. The stretch blow molding may be carried out by stretching the preform in the longitudinal direction at temperatures within the range of the stretching temperatures for the laminated structure, and further blow-molding the stretched preform to stretch it in the transverse direction (biaxial stretching blow-molding method).

For example, a polyester container may be produced in accordance with the biaxial stretching blow-molding method by stretching a bottomed parison molded by an ordinary injection-molding machine, or a parison obtained by bottoming one end of a parison molded by an extrusion molding machine at a temperature of 80 to 120 °C, preferably 90 to 110 °C, to 1.5 to 3.5 times in the longitudinal direction, and to 2 to 5 times, preferably 3 to 4.5 times in the transverse direction by a rod moving longitudinally within a blow-molding mold and the blowing of a pressurized gas. Particularly, a biaxially stretched blow-molded container as the polyester laminated blow-molded article of the invention has excellent gas-barrier property and transparency, and is suitable therefor for holding not only seasonings, oils, wines and liquors, cosmetics and detergents but also for holding sparkling drinks such as cola, cider and beer as stated hereinabove.

Table 1

Run (*)	Composition of the copolyester	Tg	P_{CO_2}	[η]
	(mole%)	(°C)	(cc.mm/m^2.day.atm)	(dl/g)
Ex. A1	IA/NDA/DER/EG 90/10/15/85	73	3.0	0.83
Ex. A2	IA/NDA/DER/EG 80/20/15/85	78	3.1	0.81
Ex. A3	IA/NDA/DER/EG 70/30/15/85	84	3.3	0.83
CEx. A1	TA/EG 100/100	78	21.8	0.75
CEx. A2	IA/EG 100/100	67	3.0	0.80
CEx. A3	NDA/EG 100/100	124	7.2	0.80
CEx. A4	IA/NDA/DER/EG 50/50/15/85	90	4.2	0.80
CEx. A5	IA/TA/EG/DER 70/30/85/15	69	3.8	0.78
CEx. A6	IA/TA/EG/DER/BSE 70/30/72/15/12	78	5.1	0.81
Ex. = Example; CEx. = Comparative Example				

The total amount of the dicarboxylic acid and the dihydroxy compound was 100 mole %.

The following abbreviations were used.

IA: isophthalic acid
NDA: 2,6-naphthalenedicarboxylic acid
TA: terephthalic acid
DER: 1,3-bis(2 hydroxyethoxy)benzene
EG: ethylene glycol
BSE: bis(4-beta-hydroxyethoxyphenyl)sulfone

EXAMPLES B1 to B6 and COMPARATIVE EXAMPLES B1 to B8

One hundred parts of polyethylene terephthalate (Mitsui PET J135, a product of Mitsui PET Resin Co., Ltd.) dried at 150 °C for 10 hours was mixed with each of the amounts indicated in Table 2 of the copolyester obtained in Example A1. The mixture was melt-extruded at a molding temperature of about 250 to 290 °C by an extruder, cooled and cut by a cutter to form pellets of a polyester composition composed of polyethylene terephthalate and the copolyester. The pellets were press-formed to prepare a press sheet having a thickness of about 600 micrometers. The press sheet was stretched simultaneously by a biaxially stretching device to three times both in the longitudinal and transverse directions to obtain a biaxially stretched film.

Table 3

Run	Composition (example designation)	Properties of the biaxially stretched bottle	
		Haze (%) of the side surface of the bottle	CO_2 gas permeation coefficient (cc/day.bottle.atm)
Ex. B7	Ex. B1	1.8	1.5
Ex. B8	Ex. B3	2.0	1.5
Ex. B9	Ex. B5	2.4	1.6
CEx. B9	CEx. B3	2.8	2.1
CEx. B10	CEx. B5	2.0	1.9
CEx. B11	CEx. B7	3.0	2.8

EXAMPLE C1

Polyethylene terephthalate (Mitsui PET J135, a product of Mitsui PET Resin Co., Ltd.) dried at 150 °C for 10 hours was press-formed at about 260 °C to prepare a press sheet having a thickness of about 100 micrometers.

Separately 100 parts of the polyethylene terephthalate was mixed with 20 parts of the copolyester of Example A1, and the mixture was melt-extruded at 260 to 280 °C by using an extruder to produce pellets of the composition. The pellets of the composition were press-formed at about 260 °C to prepare a press sheet having a thickness of about 100 micrometers. The above polyethylene terephthalate press sheet was laid over the press sheet of the composition, and the assembly was press-formed at about 260 °C to give a two-layer laminated sheet having a thickness of about 600 micrometers. The resulting laminated sheet had good adhesion between the polyethylene terephthalate layer (C) and the polyester composition layer (D) and had a haze of 1.2 %. The carbon dioxide gas permeability coefficient was 15.5 cc.mm/m^2.day.atm.

The laminated sheet was simultaneously stretched in the longitudinal and transverse direction to 3 times by a biaxially-stretching device to prepare a biaxially stretched film having a thickness of about 50 micrometers. The film was in the uniformly stretched state. The biaxially stretched film also shows good adhesion between the polyethylene terephthalate layer (C) and the polyester composition layer (D). The film had a haze of 0.6 %, and a carbon dioxide gas permeability coefficient of 10.0 cc.mm/m^2.day.atm.

EXAMPLES C2 AND C3 and COMPARATIVE EXAMPLES C1 to C4

In the same way as in Example C1, press sheets and biaxially stretched films were prepared except that the copolyesters indicated in Table 4 were used. The haze values and carbon dioxide gas permeability coefficients of the products are shown in Table 4.

to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

2. A copolyester according to claim 1 having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.6 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

3. The copolyester of claim 2 which further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

4. The copolyester of claim 2 which further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-trishydroxymethylpropane units.

5. A gas-barrier property imparting agent comprising a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

6. A gas-barrier property imparting agent according to claim 5 comprising a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.6 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

7. The gas-barrier imparting agent of claim 6 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

8. The gas-barrier property imparting agent of claim 6 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-trishydroxymethylpropane units.

9. A polyester composition comprising (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)-benzene units.

10. A polyester composition according to claim 9 comprising (A) 70 to 90 % by weight of polyethylene terephthalate and (B) 30 to 10 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.6 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

11. The polyester composition of claim 10 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

12 The polyester composition of claim 10 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-trishydroxymethylpropane units.

13. A film composed of a polyester composition comprising (A) 50 to 95 % by weight of polyethylene terephthalate and (B) 50 to 5 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.3 to 1.5 dl/g and being derived from dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

14. A film according to claim 13 which is composed of a polyester composition comprising (A) 70 to 90 % by weight of polyethylene terephthalate and (B) 30 to 10 % by weight of a copolyester having an intrinsic viscosity, measured in o-chlorophenol at 25 °C, of 0.6 to 1.0 dl/g and being derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units.

15. The film of claim 14 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

16. The film of claim 14 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the

polyethylene terephthalate layer and (D) a copolyester layer composed of a copolyester derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units or a copolyester composition comprising said copolyester and polyethylene terephthalate, said polyalkylene terephthalate layer (C) and the copolyester layer (D) being stretched.

31. The polyester stretched laminated structure of claim 30 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

32. The polyester stretched laminated structure of claim 30 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-trishydroxymethylpropane units.

33. A preform for a laminated blow-molded article, said preform being composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

34. A preform for a laminated blow-molded article according to claim 33, said preform composed of (C) a polyethylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from a dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

35. The preform of claim 34 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compound units.

36. The preform of claim 34 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-trishydroxymethylpropane units.

37. A polyester laminated blow-molded article composed of (C) a polyalkylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 95 to 60 mole % of isophthalic acid units and 5 to 40 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 95 to 70 mole % of ethylene glycol units and 5 to 30 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

38. A polyester laminated blow-molded article according to claim 37 which is composed of (C) a polyethylene terephthalate layer and (D) a copolyester layer, the copolyester layer (D) being composed of a copolyester derived from dicarboxylic acid units composed of 90 to 70 mole % of isophthalic acid units and 10 to 30 mole % of 2,6-naphthalenedicarboxylic acid units and dihydroxy compound units composed of 90 to 80 mole % of ethylene glycol units and 10 to 20 mole % of 1,3-bis(2-hydroxyethoxy)benzene units, or a copolyester composition comprising said copolyester and polyethylene terephthalate.

39. The polyester laminated blow-molded article of claim 38 in which the copolyester further comprises 0.01 to 2 mole, per 100 mole of the dihydroxy compound units, of trifunctional or higher-functional polyhydroxy compund units.

40. The polyester laminated blow-molded article of claim 38 in which the copolyester further comprises 0.05 to 1 mole, per 100 mole of the dihydroxy compound units, of 1,1,1-trishydroxymethylpropane units.

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